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(54) Title: VEGETABLE PROTEIN ADHESIVE COMPOSITIONS

(57) Abstract: Vegetable protein-based adhesive compositions and methods for preparing them are provided. The adhesives are prepared by copolymerizing hydrolyzed vegetable protein that has been functionalized with methylol groups and one or more co-monomers also having methylol functional groups. Preferred hydrolyzed vegetable proteins include hydrolyzed soy protein obtained from soy meal.

VEGETABLE PROTEIN ADHESIVE COMPOSITIONS

Related Application

This application claims priority from U.S. Provisional Application Number 60/181,938 filed February 11, 2000.

Field of the Invention

5 Vegetable protein-based adhesive compositions and methods for preparing them are provided. The adhesives are prepared by copolymerizing hydrolyzed vegetable protein that has been functionalized with methylol groups and one or more co-monomers also having methylol functional groups. Preferred hydrolyzed vegetable proteins include hydrolyzed soy protein obtained from soy meal.

Background of the Invention

10 Ancient adhesive raw material choices were limited. Starch, blood and collagen extracts from animal bones and hides were the early sources. Somewhat later, the range of raw materials used in adhesives was expanded to include milk protein and fish extracts. These early starch and protein-based adhesives suffered from a number of drawbacks. They generally lacked durability, and were able to maintain long-term strength only as long as they were kept dry.

15 Adhesives based on soyflour first came into general use during World War I. To obtain suitable soyflour for use in these early adhesives, the oil had to be extracted from soybean meal and the meal ground into to extremely fine flour. These early soybean adhesives suffered from the same drawbacks as other early protein-based adhesives, and their use was strictly limited to interior applications.

20 In the 1920's, phenol-formaldehyde and urea-formaldehyde resins were first developed. Phenol-formaldehyde and urea-formaldehyde resins are exterior-durable, in contrast to the protein-based adhesives, such as the early soyflour adhesives, in use at that time. The phenol-formaldehyde and urea-formaldehyde resins, also referred to as "thermoset" polymeric adhesives, suffered from a number of drawbacks, the foremost of which was the high cost of raw materials. These adhesives did, however, demonstrate superior durability when compared to the early protein-based adhesives. World War II perpetuated the rapid development of these adhesives for water and weather resistant applications, such as exterior applications. The low cost protein-based adhesives continued to be used in interior applications, however.

25 After World War II, the petrochemical industry invested vast sums of money in research and development to create and expand new markets for petrochemicals. Within several years, the costly raw materials used in manufacturing thermoset adhesives became inexpensive bulk commodity chemicals. In the 1960's, the price of petrochemical-based adhesives had become so low that they displaced protein adhesives out of their markets.

Summary of the Invention

30 Over the past several years, the cost of petrochemicals used as raw materials in thermoset resins have risen to the point where protein-based adhesives can compete in the same markets that are today enjoyed by the thermoset adhesives. A protein-based adhesive that combines the cost benefits of proteins as a raw material with the superior

exterior durability characteristics of thermoset adhesives is therefore desirable. In accordance with the present invention, a low cost soybean-based adhesive suitable for exterior uses is provided. The adhesive is prepared by copolymerizing hydrolyzed soybean protein and selected co-monomers currently used in thermoset adhesives.

5 In a first embodiment of the present invention, an adhesive is provided, the adhesive including a copolymer of a vegetable protein having a plurality of methylol groups and at least one co-monomer having a plurality of methylol groups.

In one aspect of the first embodiment, the vegetable protein comprises soy protein, for example hydrolyzed soy protein.

In another aspect of the first embodiment, a soymeal having a protein content of from about 40 wt. % to about 50 wt. % and an oil content of less than about 11 wt. % includes the soy protein.

10 In a further aspect of the first embodiment, the co-monomer is a methylol compound including dimethylol phenol, dimethylol urea, tetramethylol ketone, and trimethylol melamine.

In yet another aspect of the first embodiment, a composite board includes the adhesive.

15 In a second embodiment of the present invention, a method of preparing an adhesive is provided, the method including the steps of providing a denatured vegetable protein; functionalizing the denatured vegetable protein with a plurality of methylol groups, thereby yielding a methylolated vegetable protein; providing a co-monomer having a plurality of methylol groups; preparing a solution comprising the methylolated vegetable protein and the co-monomer; maintaining the solution at an elevated temperature, whereby the methylolated vegetable protein and the co-monomer polymerize; and recovering an adhesive, the adhesive comprising the polymerization product of the methylolated vegetable protein and the co-monomer.

20 In one aspect of the second embodiment, the hydrolyzed vegetable protein comprises a hydrolyzed soy protein.

In another aspect of the second embodiment, the step of providing a hydrolyzed vegetable protein includes the steps of providing a plurality of soybeans, the soybeans comprising a soy protein; processing the soybeans into soymeal; and hydrolyzing the soy protein. The step of processing the soybeans into soymeal may include subjecting the soybeans to a process selected from the group consisting of solvent extraction, extrusion, and expansion/expelling; and recovering a soymeal.

25 In a further aspect of the second embodiment, the step of denaturing the vegetable protein includes the steps of forming an aqueous, alkaline solution of the vegetable protein; and maintaining the solution at an elevated temperature, thereby producing a denatured vegetable protein. The step of forming an aqueous, alkaline solution of the vegetable protein may include forming an aqueous, alkaline solution of the vegetable protein and a phase transfer catalyst, such as polyethylene glycol, a quaternary ammonium compound, and tris(dioxa-3,6-heptyl)amine. The step of forming an aqueous, alkaline solution of the vegetable protein may also include forming an aqueous, alkaline solution of the vegetable protein and an antioxidant, such as tertiary butylhydroquinone and butylated hydroxyanisone. The step of forming an aqueous,

alkaline solution of the vegetable protein may include forming an aqueous, alkaline solution of the vegetable protein and urea.

In yet another aspect of the second embodiment, the step of functionalizing the denatured vegetable protein with a plurality of methylol groups, thereby yielding a methylolated vegetable protein includes the reacting the denatured 5 vegetable protein with formaldehyde in a basic solution at elevated temperature, thereby yielding a methylolated soy protein.

In yet a further aspect of the second embodiment, the step of providing a co-monomer having a plurality of methylol groups comprising the steps of providing a compound selected from the group consisting of phenol, urea, acetone, and melamine; and reacting the compound with formaldehyde in a basic solution at elevated temperature, thereby yielding a 10 co-monomer having a plurality of methylol groups. The step of functionalizing the denatured vegetable protein with a plurality of methylol groups and the step of providing a co-monomer having a plurality of methylol groups may be conducted in a single reaction mixture.

In yet another aspect of the second embodiment, the step of maintaining the solution at an elevated temperature, whereby the methylolated vegetable protein and the co-monomer polymerize includes maintaining the solution at an 15 elevated temperature, whereby a methylol group of the vegetable protein and a methylol group of the co-monomer undergo a condensation reaction such that a water molecule is liberated and a reactive ether linkage is formed, the ether linkage reacting such that a formaldehyde group is liberated and a methylene bridge is formed. The step of maintaining the solution at an elevated temperature may also include maintaining the solution at an elevated temperature, whereby a hydroxyl group of the vegetable protein and a methylol group of the co-monomer undergo a condensation reaction such that 20 a water molecule is liberated and a reactive ether linkage is formed, the ether linkage reacting such that a formaldehyde group is liberated and a methylene bridge is formed. The step of maintaining the solution at an elevated temperature may also include maintaining the solution at an elevated temperature, whereby an amine group of the vegetable protein and a methylol group of the co-monomer undergo a condensation reaction such that a water molecule is liberated and a methylene bridge is formed.

25 In yet another aspect of the second embodiment, the method further includes the step of providing a solid substance; mixing the solid substance with the solution; and recovering a composite. The composite may include a fiberboard. The solid substance may include an agricultural material, such as corn stalk fiber, poplar fiber, wood chips, and straw.

Detailed Description of the Preferred Embodiment

30 The following description and examples illustrate a preferred embodiment of the present invention in detail. Those of skill in the art will recognize that there are numerous variations and modifications of this invention that are encompassed

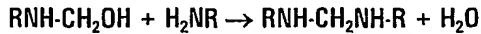
by its scope. Accordingly, the description of a preferred embodiment should not be deemed to limit the scope of the present invention.

The present invention discloses the copolymerization of soybean protein and methylolated compounds. Suitable compounds include, for example, methylolated urea, melamine, phenol, and acetone. The adhesives may be prepared using the methylolated compounds as raw materials, or else suitable compounds may be methylolated via reaction with formaldehyde as a step in the process of preparing the adhesive.

In the past, the value of crosslinking formaldehyde with a protein was to insolubilize and resinify the protein. Formaldehyde also improves the solubility and stability of the protein in the dissolved state. The adhesives of the preferred embodiments are based on a soluble protein. The soluble protein is reacted with formaldehyde to form methylol derivatives.

Methylolated proteins react with other methylolated compounds to form thermoset resins. These thermoset resins are then crosslinked to form exterior resins.

Urea and melamine, along with formaldehyde, are the basic reagents that form the common amino resins. Three reactions are involved in the formation of the resins: methylolation, condensation and methylene bridge formation. In the methylolation reaction, formaldehyde reacts with urea and melamine in the presence of an acid or base catalyst to add a methylol group to each of the molecule's primary amine groups. The secondary and primary amine groups of proteins also undergo methylolation with formaldehyde in the presence of an acid or base catalyst. In the condensation reaction, water is liberated to form a polymer chain or network. This is referred to as methylene bridge formation:



The condensation and methylene bridge formation steps result in the polymerization and crosslinking of the methylolated molecules.

The Soy Protein

One of the components of the adhesives of preferred embodiments is a protein obtained from soybeans. The soybean plant belongs to the legume family. The protein content of the soybeans is typically about 40 wt. %. After the hulls and the oil are removed from the soybean ("defatting"), the resulting product, referred to as defatted soymeal, typically has a protein content of about 40 wt. % to about 50 wt. %.

Soy meal is typically obtained from soybeans by separating all or a portion of the oil from the soybean. Soy meal is typically obtained from soybeans by solvent extraction, extrusion or expelling/expansion methods.

In solvent extraction methods, soybeans entering the processing plant are screened to remove damaged beans and foreign materials, and are then comminuted into flakes. The soybean oil is removed from the flakes by extraction with a solvent, such as hexane. Suitable extraction apparatus are well known in the art and may include, for example, countercurrent extractors. After the defatted flakes leave the extractor, any residual solvent is removed by heat and vacuum. Soymeal produced by solvent extraction methods contains essentially no oil and about 40 to 50 wt. % protein.

In extrusion methods, after the soybeans are screened and flaked, the flakes are heated under conditions of pressure and moisture in an extrusion apparatus. Suitable extrusion apparatus are well known in the art, including, for example, horizontal screw extrusion devices. Soymeal from extrusion methods typically contains about 5-9% oil and about 40-48% protein. In preferred embodiments, soybeans defatted in an extrusion process are preferred because of their lower
5 cost and because the small amount of oil left in the soymeal improves the moisture resistance of the adhesive. However, soybeans defatted in a solvent extraction process or any other process are also suitable for use in the adhesives of the preferred embodiments.

Another method for producing soymeal is the expansion/expelling method. This method has gained in popularity over other methods because of the quality of the byproducts produced, as well as the freedom from environmental hazards
10 associated with solvent extraction methods. In the expansion/expelling method, the raw soybeans are fed through a series of augers, screeners, and controlled rate feeders into the expanders. The internal expander chambers and grinders create extreme temperature and pressure conditions, typically from about 375 to about 425 psi. The oil cells of the bean are ruptured as the product, in slurry form, exits the expander and the pressure drops down to atmospheric pressure. The high frictional temperature, typically between about 150°C to about 177°C, cooks the meal and oil, yielding a high quality
15 product. About half of the 12% moisture present in the raw soybean is released as steam as the slurry exits the expander. The water and steam mix inside the expander, keeping the slurry fluid as well as aiding in the cooking process. The hot soymeal slurry is then fed to a continuous oil expeller. The meal is squeezed under pressure and the free oil is expelled. The oil and the meal are then separated and recovered. The soymeal exits the press as both a dry powder and chunks,
20 which can be milled with a hammermill to an acceptable bulk density and consistency. The product may then be passed through a cooler where heat is extracted. The final expanded/expelled soymeal typically contains about 7 to 11 % oil and about 42 to 46 % protein, on a dry matter basis. Solvent extraction of the meal produces a product typically containing less than about 0.1% oil and about 48% protein.

To produce a soymeal suitable for use in the adhesives of the preferred embodiments, it is ground into fine flour. Typically, the dry extracted meal is ground so that substantially all of the flour passes through a 65 mesh screen.

25 In preferred embodiments, the soymeal contains about 44 wt. % or more protein. However, soymeals with lower protein content may also be suitable in certain embodiments. Soymeal having various oil contents may be used in preferred embodiments.

The soy protein in soymeal is a globular protein consisting of a polypeptide chain made up of amino acids as monomeric units. Proteins typically contain 50 to 1000 amino acids residues per polypeptide chain. The amino acids are
30 joined by peptide bonds between the alpha-carboxyl groups and the alpha-amino groups of adjacent amino acids, wherein the alpha-amino group of the first amino acid residue of the polypeptide chain is free. The majority of amino acid residues in proteins tend to be hydrophobic, and as such are not very water-soluble. The molecular structures of soy proteins

contain a hydrophobic region that is enclosed within a hydrophilic region, so that many of the polar groups are unavailable. The globular shape of proteins in aqueous solution is a consequence of the fact that the proteins expose as small a surface as possible to the aqueous solvent so as to minimize unfavorable interactions with the water and maximize favorable interactions of the amino acid residues with each other. The conformation of the protein is maintained by disulfide bonds 5 and by non-covalent forces, such as van der Waals interactions, hydrogen bonds, and electrostatic interactions.

When a protein is treated with a denaturant, the conformation is lost because the denaturant interferes with the forces maintaining the configuration. The result is that more polar groups of the protein are available for reaction. In preparing the adhesives of the preferred embodiments, the soy protein is first denatured. Any suitable denaturants as are well known in the art, for example, organic solvents, detergents, concentrated urea solutions, or even heat, may be used to 10 denature the soy protein. However, in preferred embodiments, alkali or acid treatments at elevated temperatures are used to denature the protein by breaking hydrogen bonds, that is, by hydrolyzing the protein.

The denaturing of the protein is preferably performed as a separate step, however, in certain embodiments it may be conducted by adding urea or another denaturant to the soy protein methylation reaction mixture. In preferred embodiments, a phase transfer catalyst is added to the denaturing reaction mixture. The phase transfer catalyst serves to 15 enhance the rate of reaction occurring in a two phase organic-aqueous system by catalyzing the transfer of water soluble reactants across the interface to the organic phase. Suitable phase transfer catalysts include polyethylene glycol, quaternary ammonium compounds, and the like. In a preferred embodiment, the phase transfer catalyst is tris(dioxa-3,6-heptyl)amine, commonly referred to as Thanamine or TDA-1 (available from Rhodia, Inc. of Cranbury, New Jersey). In various embodiments, it is preferred to add a component to the reaction mixture that enhances the solubility of the protein, 20 thereby facilitating the denaturing reaction. Certain antioxidants, including tertiary-butylhydroquinone (TBHQ) and butylated hydroxyanisole (BHA), are observed to increase the solubility of soy protein, however, other suitable solubility enhancers may also be used.

Because of its low cost, it is preferred to use soymeal as the source of vegetable protein in the adhesives of the preferred embodiments. However, it is to be understood that the adhesives of the preferred embodiments are not limited to 25 only those prepared from soy protein. Other sources of vegetable protein are also suitable for use in preferred embodiments. Non-limiting examples of other sources of vegetable protein include, for example, nuts, seeds, grains, and legumes. These sources include, but are not limited to, peanuts, almonds, brazil nuts, cashews, walnuts, pecans, hazel nuts, macadamia nuts, sunflower seeds, pumpkin seeds, corn, peas, wheat, and the like. Additional and/or different processing steps from those used to prepare the soymeal of preferred embodiments may be used in refining and separating 30 the protein from the raw product of these other sources, as will be appreciated by one skilled in the art. The processed proteins, after being subjected to a denaturing step, may be methylolated according to the methods illustrated below for

soymeal, and may be reacted with methylolated co-monomers as illustrated below for soymeal to produce adhesives acceptable for various applications.

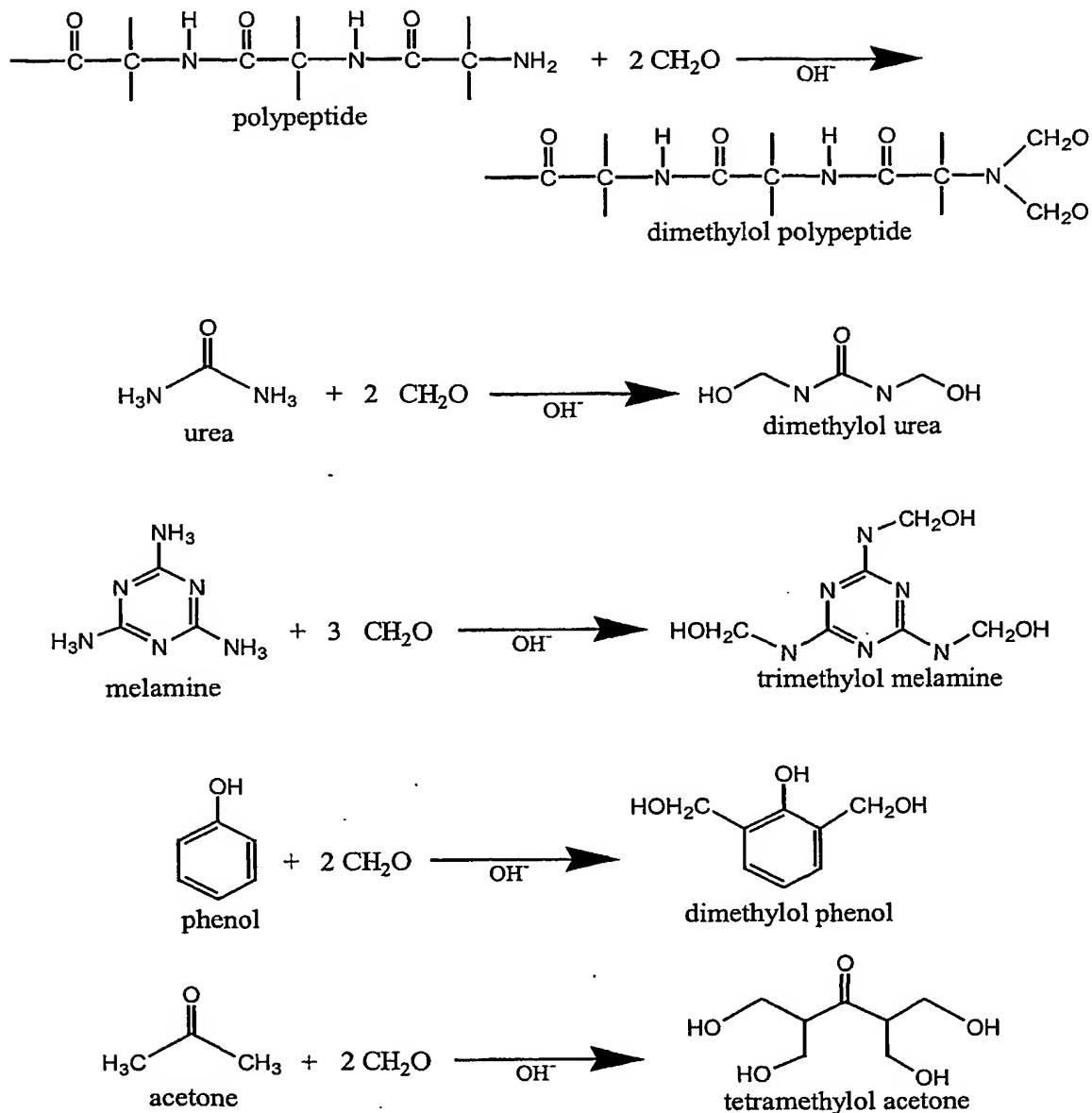
The Co-Monomer(s)

To prepare the adhesives of the preferred embodiments, the soy protein and one or more co-monomers are 5 polymerized. In order for the polymerization reaction to occur, the soy protein is first subjected to methylation. If the co-monomers do not already contain methylol groups, they too are subjected to methylation prior to the polymerization reaction. Preferred co-monomers include any molecule containing methylol groups, or any molecule which may undergo methylation, for example, via reaction with formaldehyde. Non-limiting examples of suitable methylol-containing molecules include dimethylol urea, trimethylol melamine, tetramethylol ketone and dimethylol phenol. Nonlimiting examples 10 of suitable co-monomers capable of undergoing methylation via reaction with formaldehyde include urea, melamine, and phenol. In preferred embodiments, the co-monomer is capable of substitution by two, three, four or more methylol groups. Generally, co-monomers having more methylol substituents are more reactive than co-monomers having fewer methylol substituents.

A single co-monomer or mixtures of two or more co-monomers may be used in the adhesives of the preferred 15 embodiments. A preferred co-monomer mixture contains methylol ketone and methylol phenol. Different co-monomers possess different properties and characteristics. By combining two or more co-monomers having different characteristics, an adhesive having properties that render it especially suitable for a particular application may be obtained.

The Methylation Reaction

The first step in the preparation of the adhesives of the preferred embodiment involves methylation (also 20 referred to as hydroxymethylation) of the denatured protein's polypeptide chain, along with methylation of any of the co-monomers that do not already incorporate methylol groups. Any suitable reaction may be used to functionalize the protein or co-monomer with hydroxymethyl groups. In preferred embodiments, however, the methylation reaction proceeds by reacting the protein or co-monomer with formaldehyde in the presence of an acid or base catalyst. The methylation of the protein and the co-monomer(s) may be conducted simultaneously in the same reaction mixture, or may be conducted 25 separately for each component. Methylation of proteins and amines such as urea and melamine typically involves substitution of primary and/or secondary aminic hydrogens by hydroxymethyl groups. When the co-monomer is phenol, the methylation reaction involves replacing the phenol molecule's two ortho hydrogens or an ortho hydrogen and a para hydrogen with hydroxymethyl groups. The reaction yields a mixture of 2,4-dimethylol phenol and 2,6-dimethylol phenol. When the co-monomer is acetone, a methyl hydrogen is replaced by a hydroxymethyl group. Typical methylation 30 reactions for a polypeptide and selected co-monomers of the preferred embodiments are illustrated below.



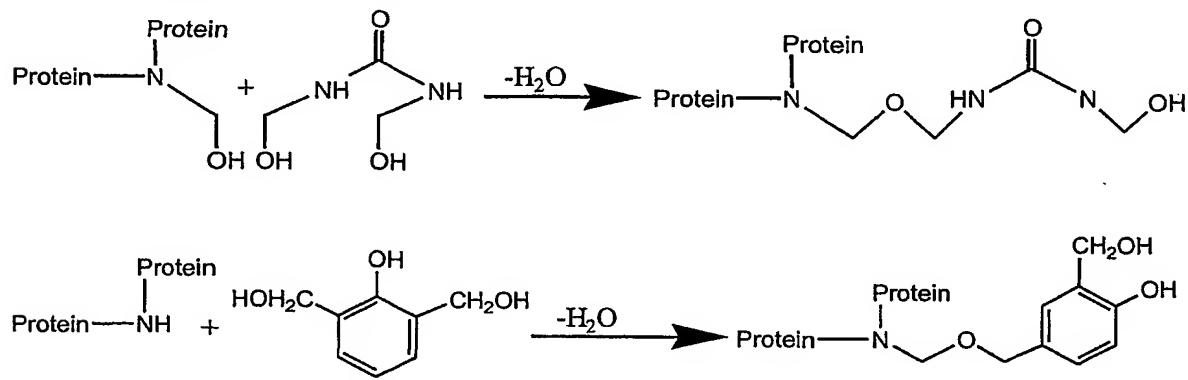
hours are typically sufficient to ensure complete methylation. However, as will be appreciated by one skilled in the art, the methylation reaction may proceed more rapidly or more slowly in certain embodiments, resulting in a shorter or longer reaction time.

Methylation of the polypeptide chains of the soy protein and the non-methylated or partially-methylated co-monomer may preferably be conducted at the same time in the same reaction mixture, so as to provide a simpler process. However, the methylation of the polypeptide chains of the soy protein may be conducted separately from that of the non-methylated or partially-methylated co-monomer in certain embodiments.

Copolymerization

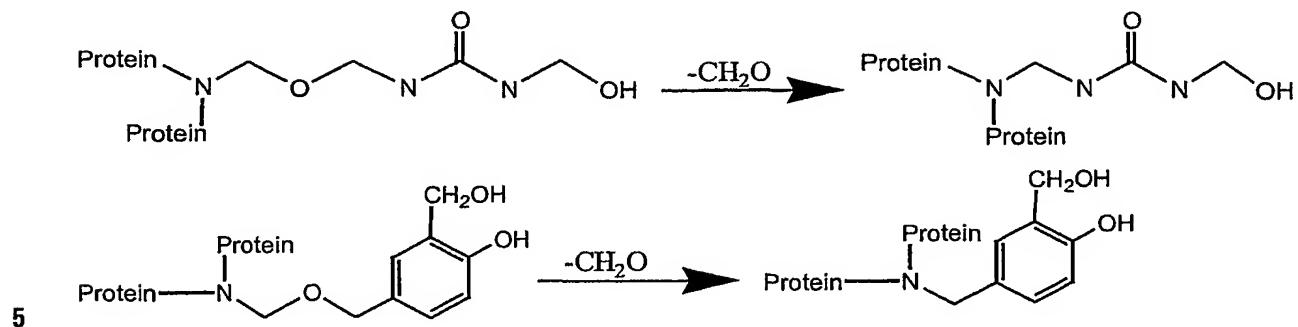
After methylation of the soy protein and, if necessary, the co-monomer, the next step in the preparation of the adhesives of the preferred embodiments involves polymerization (also referred to as resinification or curing) of the protein and co-monomer molecules. One of the reactions in the polymerization process involves the condensation of a methylol group with an amine group to liberate water and form a methylene bridge. Another reaction in this process involves condensation of two methylol groups to yield an unstable ether linkage, which undergoes a reaction to liberate formaldehyde, thereby forming a methylene bridge. This free formaldehyde then reacts with the reactive amine groups of the polypeptide to form additional methylol groups. Methylol groups are also capable of condensing with non-methylated hydroxyl groups to form unstable ether linkages.

Because each protein molecule typically contains methylol groups and groups that are reactive to methylol groups, significant crosslinking occurs. In preferred embodiments, the reaction is conducted at elevated temperature. Preferred temperatures are typically between 65°C and 110°C. However, higher or lower temperatures may be preferred in certain embodiments, as will be appreciated by one skilled in the art. Typical condensation reactions between a methylolated protein and either a 2,6-methylolated urea or 2,6-dimethylol phenol are depicted below.



As stated above, the ether linkages formed in certain of the condensation reactions are not stable. At elevated temperatures or under acidic conditions, formaldehyde is spontaneously liberated from the linked molecules to yield a methylene bridge. The released formaldehyde may then participate in further methylation reactions. The formation of the

methylene bridge in a methylolated protein molecule coupled to either methylolated urea or methylolated phenol is depicted below.



Use of Adhesives in Composition Boards

The adhesives of preferred embodiments are suitable for use in a variety of applications, including applications where conventional resin adhesives are typically used. One particularly preferred application for the adhesives of the 10 preferred embodiments is in the manufacture of composition boards. Composition boards prepared using the soy protein based adhesives of the preferred embodiments possess acceptable physical properties as set forth in industry standards.

The physical properties of composition boards are measured according to standards set forth by the American Society for Testing and Materials in "Standards and Methods of Evaluating the Properties of Wood-Base Fiber and Particle Panel Materials." Two of the more significant physical properties of finished composition board include modulus of 15 elasticity and modulus of rupture under static bending conditions. Modulus of elasticity is a measure of the stiffness of the sample and is reported in pounds per square inch (psi) or Pascals (Pa). Modulus of rupture is regarded as the breaking strength of the sample and is reported in psi or Pa. In composition boards, both of these properties are determined parallel to the face of the panel. The acceptable range for modulus of rupture will vary depending upon the grade of composition board. For board having a thickness of one half inch, the modulus of rupture is preferably within the range of 1000 psi to 20 3000 psi, however for certain embodiments values outside of this range may also be acceptable.

Another property, tensile strength perpendicular to the surface, also referred to as internal bond, provides a measure of how well the board is glued together. The value is reported in psi or Pa. The acceptable range for internal bond will vary depending upon the grade of composition board. The internal bond is preferably from about 35 psi to about 100 psi for board having a thickness of one half inch. However, for certain embodiments values outside of this range may also be acceptable. This test is currently not used extensively, but should become more important as the composition board industry moves towards greater production of boards for use in structural applications.

Water resistance is evaluated by submerging a sample of board in water at room temperature for 24 hours and by submerging another sample in boiling water for 2 hours. Typically, only the 24 hour test is conducted, unless the panel is

to be used in structural or construction applications. In the water resistance test, the thickness of the board is measured before and after submerging the sample in water. The thickness swell is then measured as the percent increase in thickness. Acceptable water resistance is typically indicated by a thickness swell of less than about 15%, however for certain embodiments values outside of this range may also be acceptable.

5

Examples

Adhesives Prepared from Untreated Soymeal

Adhesives were prepared from untreated soymeal and resins including urea and formaldehyde, melamine, and phenol formaldehyde.

10

Example 1

Soymeal with urea and formaldehyde

Component	Wt. (g)
Soymeal (44% protein, 5-6% oil)	200
Sodium hydroxide	16
Water	536
Polyethylene glycol 400 (phase transfer catalyst)	6
Urea	60
Aqueous solution of 37 wt. % formaldehyde and 7 wt. % MeOH	138
Sodium silicate	20
Total	976

The sodium hydroxide, water and polyethylene glycol were mixed together and heated to 80°C. 100 grams of the untreated soybean meal were added to the mixture, then approximately ten minutes later the remaining soybean meal was added. The soybean meal underwent hydrolysis under the basic reaction conditions. An antifoam agent and formaldehyde solution were added, after which the temperature of the mixture was approximately 62°C. The temperature was raised to 90°C over the course of approximately 30 minutes, and maintained at 90°C for approximately 20 minutes. The mixture was allowed to cool, and the pH was adjusted to 8.5 with formic acid. The percentage of solids in the mixture was 36.4%. The sodium silicate was added to the mixture, which raised the pH to 9.9. The mixture was subjected to vacuum distillation at an elevated temperature of approximately 65-67°C. After vacuum distillation, the resin had a pH of 9.8, a viscosity of 1227 cps (measured at 20 rpm, spindle #64, using a Brookfield-Model DV-E viscometer), and a solids content of 50.5%.

15

The resin was allowed to cure by placing it in an oven at a temperature of 110°C for 2 hours, then a 5 g sample of the cured resin was placed in 80 g of boiling water for 0.5 hours. In contrast to typical urea resins which tend to break

down in boiling water and emit free formaldehyde to the atmosphere, the soymeal-urea resin was insoluble in the boiling water.

Example 2

Soymeal with melamine

Component	Wt. (g)
Soymeal (44% protein, 5-6% oil)	200
Sodium hydroxide	16
Water	536
Polyethylene glycol 400 (phase transfer catalyst)	6
Melamine	39
Aqueous solution of 37 wt. % formaldehyde and 7 wt. % MeOH	76
Total	873

5

The sodium hydroxide, water and polyethylene glycol were mixed together and heated to 80°C. 100 grams of the soybean meal was added to the mixture, eight minutes later an additional 50 grams of soybean meal was added, then four minutes later the remaining soybean meal was added. During the soybean meal addition, the mixture was heated to 105°C. The mixture was then cooled to 80°C, the melamine was added, and then the formaldehyde solution was added. The temperature of the mixture was maintained at 80°C for approximately 5 minutes, then allowed to cool to 60°C over the course of approximately 1.25 hours. The mixture was subjected to vacuum distillation at a temperature of approximately 60°C. After vacuum distillation, the resin had a pH of 12.0, a viscosity of 3180 cps (measured at 20 rpm, spindle #64, using a Brookfield-Model DV-E viscometer), and a solids content of 49.3%.

10

The resin was cured as in Example 1, and a 5 g sample was placed in 80 g boiling water for 0.5 hours. The 15 soymeal-melamine resin was insoluble in the boiling water.

Example 3**Soymeal with phenol and formaldehyde**

Component	Wt. (g)
Soymeal (44% protein, 5-6% oil)	200
Sodium hydroxide	16
Water	536
Polyethylene glycol 460 (phase transfer catalyst)	6
Phenol (90 wt. % aq. soln.)	94
Aqueous solution of 37 wt. % formaldehyde and 7 wt. % MeOH	175
Total	1027

The sodium hydroxide, water and polyethylene glycol were mixed together and heated to 80°C. 80 grams of the 5 soybean meal were added to the mixture, an additional 40 grams of soybean meal were added, and then the remaining soybean meal was added. During the soybean meal addition, the mixture was heated to 100°C. The phenol and the formaldehyde solutions were added, after which the temperature of the mixture dropped to approximately 90-93°C. The solids content of the mixture was 33.6%. The mixture was subjected to vacuum distillation for approximately 80 minutes, yielding a mixture with solids content of 51.4 %.

10 The resin was cured as in Example 1, and a 5 g sample was placed in 80 g boiling water for 0.5 hours. The soymeal-phenol formaldehyde resin was insoluble in the boiling water.

Preparation of Soy Protein Hydrolysate

Soy protein hydrolysate, rather than untreated soymeal, was used as a starting material in various adhesives of the preferred embodiments. The soybean meal was produced by the expelling/expansion method. The protein content of 15 soybean meal produced by this method typically is from about 40 to about 48%, and the oil content from about 5 to about 11%. The presence of the oil increases the water resistance of the resulting soybean protein adhesive.

Example 4**Hydrolyzed Soymeal - 0.33 wt. % Urea**

Component	Wt. (g)
Soymeal (44% protein, 8.9% oil) (50 wt. % aq. soln., Van Waters & Rogers, Inc., Kirkwood, WA)	400
Sodium hydroxide (antioxidant, Aldrich, Milwaukee, WI)	64
Water	1040
Tris(dioxa-3,6-heptyl)amine (phase transfer catalyst, Rhodia, Inc., Cranbury, NJ)	0.04
Tertiary-butylhydroquinone (TBHQ) (antioxidant, Aldrich, Milwaukee, WI)	0.04
Butylated hydroxyanisone (BHA) (antioxidant, Aldrich, Milwaukee, WI)	0.04
Urea	5
Total	1509.1

The components were mixed together and heated to 140°C for 2 hours to form a solution. The pH of the resulting solution
5 was 10.3 and the viscosity was 650 cps (measured at 20 rpm, spindle #2, using a Brookfield-Model DV-E viscometer).

Example 5**Hydrolyzed Soymeal - 2.0 wt. % Urea**

Component	Wt. (g)
Soymeal (44 wt. % protein, 8.9 wt. % oil)	400
Sodium hydroxide (50 wt. % aq. soln.)	64
Water	1040
Tris(dioxa-3,6-heptyl)amine (phase transfer catalyst)	0.04
Tertiary-butylhydroquinone (TBHQ) (antioxidant)	0.04
Butylated hydroxyanisone (BHA) (antioxidant)	0.04
Urea	30
Total	1534.1

The components were mixed together and heated to 85°C for 30 minutes to form a solution. The pH of the
10 resulting solution was 10.3.

The antioxidants are observed to increase the solubility of the soymeal in solution. Urea is observed to decrease the water holding capacity of the protein and to decrease the viscosity of the solution. At increased urea concentrations, temperature and reaction time of the hydrolysis reaction may be decreased without significantly affecting the physical characteristics of the hydrolyzed soymeal.

5 The length of the polypeptide chains in the protein hydrosylate after hydrolysis of the soymeal is a function of pH, temperature, and time. Generally, the higher the pH or temperature, or the greater the length of time to which the soybean meal is subjected to hydrolysis, the shorter the polypeptide chain length. Typically, solutions including shorter, lower molecular weight polypeptide chains will have a lower viscosity. Depending upon the application in which the adhesive is used, lower or higher molecular weight polypeptide chains are preferred. For example, different molecular weights may be
10 preferred for different panel grades of composite boards.

Example 6

Adhesive from protein hydrosylate and tetramethylol ketone

Component	Wt. (g)
Soy protein hydrosylate (prepared according to Example 4)	1419.3
Tetramethylol ketone (approx. 3% free formaldehyde) (marketed as AF-3600 by Dynachem, Georgetown, IL)	227.4
Total	1646.7

15 The components were mixed together, and then the pH was adjusted to 9.43 with a 50 wt. % aqueous solution of NaOH. The mixture was heated to approximately 95-100°C and allowed to reflux for 17 minutes. The mixture was then cooled to 45°C and the pH adjusted to 8.5 with glacial acetic acid, after which it was vacuum distilled to 50 wt. % solids. The conditions of the vacuum distillation were 27.5 inches Hg at a temperature of 52°C.

Example 7

Protein hydrosylate with methylol phenol resin

Component	Wt. (g)
Soy protein hydrosylate (prepared according to Example 4)	1152
Dimethylol phenol (marketed as Phenalloy 2175 by Dynachem, Georgetown, IL)	506.9
Total	1658.6

20

The components were mixed together, and then the pH was adjusted to 10 with a 50 wt. % aqueous solution of NaOH. The mixture was heated to approximately 95-100°C and allowed to reflux for approximately half an hour. The mixture was cooled and the pH adjusted with acid. The mixture was then vacuum distilled to 40 wt. % solids. The conditions of the vacuum distillation were 27.5 inches Hg at a temperature of 52°C.

5

Example 8**Protein hydrosylate with methylol urea resin**

Component	Wt. (g)
Soy protein hydrosylate (prepared according to Example 4)	1200
Dimethylol urea (Dynachem, Georgetown, IL)	486
Tetramethylol ketone	57.3
Total	1743.3

The components were mixed together, and then the pH was adjusted to 9.43 with a 50% solution of aqueous NaOH. The mixture was heated to approximately 95-100°C and allowed to reflux for 66 minutes. The mixture was cooled 10 and the pH adjusted with acid. The mixture was then vacuum distilled to 40 wt. % solids. The mixture was then vacuum distilled to 40 wt. % solids. The conditions of the vacuum distillation were 27.5 inches Hg at a temperature of 52°C.

Example 9**Protein hydrosylate with methylol melamine resin**

Component	Wt. (g)
Soy protein hydrosylate (prepared according to Example 4)	1152
Trimethylolmelamine (Dynachem, Georgetown, IL)	814.6
Total	1966.6

15 The components were mixed together, and then the pH was adjusted to 10.5 with a 50% solution of aqueous NaOH. The mixture was heated to approximately 95-100°C and allowed to reflux for 67 minutes. The mixture was cooled and the pH adjusted with acid. The mixture was then vacuum distilled to 40% solids. The conditions of the vacuum distillation were 27.5 inches Hg at a temperature of 52°C.

Example 10**Protein hydrosylate with methylol ketone resin**

Component	Wt. (g)
Soy protein hydrosylate (prepared according to Example 4)	1300
Tetramethylol ketone	621.5
Total	1921.5

5 The components were mixed together, and then the pH was adjusted to 10.5 with a 50% solution of aqueous NaOH. The mixture was heated to approximately 95-100°C and allowed to reflux for 28 minutes. The mixture was cooled and the pH adjusted with acid. The mixture was then vacuum distilled to 40% solids. The conditions of the vacuum distillation were 27.5 inches Hg at a temperature of 52°C.

Example 11**Protein hydrosylate with methylol ketone and methylol phenol resin**

Component	Wt. (g)
Soy protein hydrosylate (prepared according to Example 4)	1509
Tetramethylol ketone	227
Dimethylol phenol	142
Total	1878

10

The components were mixed together, and then the pH was adjusted to 10.0 with a 50% solution of aqueous NaOH. The mixture was heated to approximately 80-95°C and allowed to reflux for 11 minutes. The mixture was cooled, the pH adjusted with acid, and then the mixture was subjected to vacuum distillation. The conditions of the vacuum distillation were 27.5 inches Hg at a temperature of 52°C.

15

Example 12**Protein hydrosylate with methylol ketone resin**

Component	Wt. (g)
Soy protein hydrosylate (prepared according to Example 2)	1300
Dimethylol urea	651
Total	1951

The components were mixed together, and then the pH was adjusted to 10.3 with a 50 wt. % solution of aqueous NaOH. The mixture was heated to approximately 100-107°C and allowed to reflux for 28 minutes. The mixture

was cooled and the pH adjusted with acid. The mixture was then vacuum distilled to 50% solids. The conditions of the vacuum distillation were 27.5 inches Hg at a temperature of 52°C. Composition Boards Containing Soy Protein Hydrolysate Adhesives

Medium density fiberboard panels were prepared using various soybean based adhesives.

5

Example 13

A medium density fiberboard panel of 0.5 inch thickness was prepared from a fiber mixture containing 50 wt. % corn stalk fiber and 50 wt. % hybrid poplar fiber. The fibers were bonded with a resin comprising a copolymer of hydrolyzed soybean protein (75.5 wt. %) and tetramethylol ketone (24.5 wt. %). The panel contained 8 wt. % of the resin and 1 wt. % wax (Borden Chemical, Waverly, VA).

10

Modulus of rupture (MOR), modulus of elasticity (MOE), internal bond (IB), and thickness swelling (TS) were measured for two samples of the panel. The test results are presented in Table 1. The data demonstrate that composition boards prepared from a resin comprising a copolymer of hydrolyzed soybean protein and tetramethylol ketone provides satisfactory modulus of rupture, modulus of elasticity, internal bond, and thickness swelling, making such panels suitable for exterior use.

15

Example 14

A medium density fiberboard panel of 0.5 inch thickness was prepared from a fiber mixture containing 50 wt. % corn stalk fiber and 50 wt. % hybrid poplar fiber. The fibers were bonded with a resin comprising a copolymer of hydrolyzed soybean protein (50 wt. %) and dimethylol phenol (50 wt. %). The panel contained 12 wt. % of the resin and 1 wt. % wax.

20

Two samples of the panel were tested as in Example 13. The test results are presented in Table 1. The data demonstrate that composition boards prepared from a resin comprising a copolymer of hydrolyzed soybean protein and dimethylol phenol provides satisfactory modulus of rupture, modulus of elasticity, internal bond, and thickness swelling, making such panels suitable for exterior use. Composite boards prepared using dimethylol phenol, a cheaper starting material than certain of the other methylol co-monomers, have the added benefit of reduced cost.

25

Example 15

A medium density fiberboard panel of 0.5 inch thickness was prepared from a fiber mixture containing 50 wt. % corn stalk fiber and 50 wt. % hybrid poplar fiber. The fibers were bonded with a resin comprising a copolymer of hydrolyzed soybean protein (50 wt. %) and dimethylol urea (45 wt. %) and tetramethylol ketone (5 wt. %). The panel contained 12 wt. % of the resin and 1 wt. % wax.

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Two samples of the panel were tested as in Example 13. The test results are presented in Table 1. Composite boards prepared using urea have little water resistance, resulting in a board that will release formaldehyde when exposed to water under room temperature conditions. In contrast, boards prepared from dimethylol urea are water resistant and do

not release formaldehyde. The data demonstrate that composition boards prepared from a resin comprising a copolymer of hydrolyzed soybean protein, dimethylol urea, and tetramethylol ketone provides satisfactory modulus of rupture, modulus of elasticity, internal bond, and thickness swelling, making such panels suitable for exterior use. The resin is especially preferred in applications where water resistance is less important and no formaldehyde emissions are desired, such as, for
5 example, interior applications.

Example 16

A medium density fiberboard panel of 0.5 inch thickness was prepared from a fiber mixture containing 50 wt. % corn stalk fiber and 50 wt. % hybrid poplar fiber. The fibers were bonded with a resin comprising a copolymer of hydrolyzed soybean protein (50 wt. %) and trimethylol melamine (50 wt. %). The panel contained 12 wt. % of the resin
10 and 1 wt. % wax.

Two samples of the panel were tested as in Example 13. The test results are presented in Table 1. The data demonstrate that composition boards prepared from a resin comprising a copolymer of hydrolyzed soybean protein and trimethylol melamine provides satisfactory modulus of rupture, modulus of elasticity, internal bond, and thickness swelling, making such panels suitable for exterior use. The good modulus of rupture, modulus of elasticity and water resistance
15 make this resin preferred for surface applications.

Example 17

A medium density fiberboard panel of 0.5 inch thickness was prepared from a fiber mixture containing 50 wt. % corn stalk fiber and 50 wt. % hybrid poplar fiber. The fibers were bonded with a resin comprising a copolymer of hydrolyzed soybean protein (50 wt. %) and tetramethylol ketone (50 wt. %). The panel contained 12 wt. % of the resin
20 and 1 wt. % wax.

Two samples of the panel were tested as in Example 13. The test results are presented in Table 1. The data demonstrate that composition boards prepared from a resin comprising a copolymer of hydrolyzed soybean protein and tetramethylol ketone provides satisfactory modulus of rupture, modulus of elasticity, internal bond, and thickness swelling, making such panels suitable for exterior use.

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Example 18

A medium density fiberboard panel of 0.5 inch thickness was prepared from a fiber mixture containing 50 wt. % corn stalk fiber and 50 wt. % hybrid poplar fiber. The fibers were bonded with a resin comprising a copolymer of hydrolyzed soybean protein (50 wt. %) and a mixture of tetramethylol ketone (25 wt. %) and dimethylol phenol (25 wt. %). The panel contained 12 wt. % of the resin and 1 wt. % wax.

30

Two samples of the panel were tested as in Example 13. The test results are presented in Table 1. The data demonstrate that composition boards prepared from a resin comprising a copolymer of hydrolyzed soybean protein,

tetramethylol ketone, and dimethylol phenol provides satisfactory modulus of rupture, modulus of elasticity, internal bond, and thickness swelling, making such panels suitable for exterior use.

Example 19

A medium density fiberboard panel of 0.5 inch thickness was prepared from a fiber mixture containing 50 wt. %
5 corn stalk fiber and 50 wt. % hybrid poplar fiber. The fibers were bonded with a resin comprising a copolymer of hydrolyzed soybean protein (50 wt. %, prepared as in Example 5) and tetramethylol ketone (50 wt. %). The panel contained 12 wt. % of the resin and 1 wt. % wax.

Two samples of the panel were tested as in Example 13. The test results are presented in Table 1. The data demonstrate that composition boards prepared from a resin comprising a copolymer of hydrolyzed soybean protein and
10 tetramethylol ketone provides satisfactory modulus of rupture, modulus of elasticity, internal bond, and thickness swelling, making such panels suitable for exterior use.

Table 1.

Example	Composition of Resin	Resin (wt. %)	Wax (wt. %)	Density (lbs/ft ³)	Sample	MOR (psi)	MOE (psi)	IB (psi)	24 hr. Soak		2 hr. Boil	
									TS (%)	Water Absorption (%)	TS (%)	Water Absorption (%)
13	Hydrolyzed soy protein (75.5 wt. %) and methylol ketone (24.5 wt. %)	8	1	42	a	2351	396688	36	54.72	128.35	146.01	193.37
14	Hydrolyzed soy protein (50 wt. %) and dimethylol phenol (50 wt. %)	12	1	43	b	2117	391083	32	57.05	128.89	167.69	205.28
15	Hydrolyzed soy protein (50 wt. %), dimethylol urea (25 wt. %), and tetramethylol ketone (25 wt. %)	12	1	43	a	4350	530021	86	25.3	82.26	44.18	99.84
					b	4250	527407	82	28.75	81.19	46.59	99.81
16	Hydrolyzed soy protein (50 wt. %) and trimethylol melamine (50 wt. %)	12	1	43	a	3148	494121	47	27.28	76.29	94.87	173.77
					b	2687	4559454	46	34.47	96.64	100.47	168.12
17	Hydrolyzed soy protein (60 wt. %) and tetramethylol ketone (40 wt. %)	12	1	43	a	3133	431153	62	25.4	94.98	49.49	112.54
					b	3203	452664	61	26.72	96.26	51.07	111.94
18	Hydrolyzed soy protein (50 wt. %), tetramethylol ketone (25 wt. %), and dimethylol phenol (50 wt. %)	12	1	43	a	4469	590098	109	13.56	48.74	38.98	91.26
					b	3957	554530	91	14.68	52.47	37.1	91.84
19	Hydrolyzed soy protein (50 wt. %), tetramethylol ketone (25 wt. %), and dimethylol phenol (50 wt. %)	12	1	43	a	3463	420766	64	21.8	82.35	31.78	91.26
					b	3469	465969	62	19.51	73.83	30.57	91.84

The above description discloses several methods and materials of the present invention. This invention is susceptible to modifications in the methods and materials, as well as alterations in the fabrication methods and equipment. Such modifications will become apparent to those skilled in the art from a consideration of this disclosure or practice of the invention disclosed herein. Consequently, it is not intended that this invention be limited to the specific embodiments disclosed herein, but that it cover all modifications and alternatives coming within the true scope and spirit of the invention as embodied in the attached claims.

WHAT IS CLAIMED IS:

1. An adhesive, the adhesive comprising a copolymer of a vegetable protein having a plurality of methylol groups and at least one co-monomer having a plurality of methylol groups.
2. The adhesive of claim 1, wherein the vegetable protein comprises soy protein.
- 5 3. The adhesive of claim 2, wherein the soy protein comprises hydrolyzed soy protein.
4. The adhesive of claim 2, wherein a soymeal having a protein content of from about 40 wt. % to about 50 wt. % and an oil content of less than about 11 wt. % comprises the soy protein.
5. The adhesive of claim 1, wherein the co-monomer is a methylol compound selected from the group consisting of dimethylol phenol, dimethylol urea, tetramethylol ketone, and trimethylol melamine.
- 10 6. A composite board comprising the adhesive of claim 1.
7. A method of preparing an adhesive, the method comprising the steps of:
providing a denatured vegetable protein;
functionalizing the denatured vegetable protein with a plurality of methylol groups, thereby yielding a methylolated vegetable protein;
- 15 providing a co-monomer having a plurality of methylol groups;
preparing a solution comprising the methylolated vegetable protein and the co-monomer;
maintaining the solution at an elevated temperature, whereby the methylolated vegetable protein and the co-monomer polymerize; and
recovering an adhesive, the adhesive comprising the polymerization product of the methylolated vegetable protein and the co-monomer.
- 20 8. The method of claim 7, wherein the hydrolyzed vegetable protein comprises a hydrolyzed soy protein.
9. The method of claim 8, wherein the step of providing a hydrolyzed vegetable protein comprises the steps of:
providing a plurality of soybeans, the soybeans comprising a soy protein;
25 processing the soybeans into soymeal; and
hydrolyzing the soy protein.
10. The method of claim 9, wherein the step of processing the soybeans into soymeal comprises:
subjecting the soybeans to a process selected from the group consisting of solvent extraction, extrusion, and expansion/expelling; and
30 recovering a soymeal.
11. The method of claim 7, wherein the step of denaturing the vegetable protein comprises the steps of:
forming an aqueous, alkaline solution of the vegetable protein; and

maintaining the solution at an elevated temperature, thereby producing a denatured vegetable protein.

12. The method of claim 11, wherein the step of forming an aqueous, alkaline solution of the vegetable protein comprises forming an aqueous, alkaline solution of the vegetable protein and a phase transfer catalyst.

13. The method of claim 12, wherein the phase transfer catalyst is selected from the group consisting of a
5 polyethylene glycol, a quaternary ammonium compound, and tris(dioxa-3,6-heptyl)amine.

14. The method of claim 11, wherein the step of forming an aqueous, alkaline solution of the vegetable protein comprises forming an aqueous, alkaline solution of the vegetable protein and an antioxidant.

15. The method of claim 14, wherein the antioxidant is selected from the group consisting of tertiary butylhydroquinone and butylated hydroxyanisone.

10 16. The method of claim 11, wherein the step of forming an aqueous, alkaline solution of the vegetable protein comprises forming an aqueous, alkaline solution of the vegetable protein and urea.

17. The method of claim 7, wherein the step of functionalizing the denatured vegetable protein with a plurality of methylol groups, thereby yielding a methylolated vegetable protein comprises the reacting the denatured vegetable protein with formaldehyde in a basic solution at elevated temperature, thereby yielding a methylolated soy
15 protein.

18. The method of claim 7, the step of providing a co-monomer having a plurality of methylol groups comprising the steps of:

20 providing a compound selected from the group consisting of phenol, urea, acetone, and melamine; and
reacting the compound with formaldehyde in a basic solution at elevated temperature, thereby yielding a co-monomer having a plurality of methylol groups.

19. The method of claim 7, wherein the step of functionalizing the denatured vegetable protein with a plurality of methylol groups and the step of providing a co-monomer having a plurality of methylol groups are conducted in a single reaction mixture.

25 20. The method of claim 7, wherein the step of maintaining the solution at an elevated temperature, whereby the methylolated vegetable protein and the co-monomer polymerize comprises maintaining the solution at an elevated temperature, whereby a methylol group of the vegetable protein and a methylol group of the co-monomer undergo a condensation reaction such that a water molecule is liberated and a reactive ether linkage is formed, the ether linkage reacting such that a formaldehyde group is liberated and a methylene bridge is formed.

30 21. The method of claim 7, wherein the step of maintaining the solution at an elevated temperature, whereby the methylolated vegetable protein and the co-monomer polymerize comprises maintaining the solution at an elevated temperature, whereby a hydroxyl group of the vegetable protein and a methylol group of the co-monomer undergo

a condensation reaction such that a water molecule is liberated and a reactive ether linkage is formed, the ether linkage reacting such that a formaldehyde group is liberated and a methylene bridge is formed.

22. The method of claim 7, wherein the step of maintaining the solution at an elevated temperature, whereby the methylolated vegetable protein and the co-monomer polymerize comprises maintaining the solution at an elevated temperature, whereby an amine group of the vegetable protein and a methylol group of the co-monomer undergo a condensation reaction such that a water molecule is liberated and a methylene bridge is formed.

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23. The method of claim 7, further comprising the step of:
providing a solid substance;
mixing the solid substance with the solution; and
recovering a composite.

24. The method of claim 13, wherein the composite comprises a fiber board.
25. The method of claim 13, wherein the solid substance comprises an agricultural material.
26. The method of claim 25, wherein the agricultural material is selected from the group consisting of corn stalk fiber, poplar fiber, wood chips, and straw.

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(54) Title: VEGETABLE PROTEIN ADHESIVE COMPOSITIONS

(57) Abstract: Vegetable protein-based adhesive compositions and methods for preparing them are provided. The adhesives are prepared by copolymerizing hydrolyzed vegetable protein that has been functionalized with methylol groups and one or more co-monomers also having methylol functional groups. Preferred hydrolyzed vegetable proteins include hydrolyzed soy protein obtained from soy meal.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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B. FIELDS SEARCHED

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE CHEMABS 'Online! chemical abstracts service, columbus, ohio, us; retrieved from STN Database access no. 51:79307 , IACHAN ABRAHAO ET AL.: "Utilization of residues of proteinic nature. I. New process of plastification of proteins." XP002172009 abstract & REV. QUIM. IND., vol. 25, no. 295, 1956, pages 13-17, Rio de Janeiro</p> <p>---</p> <p style="text-align: center;">-/--</p>	1,5

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE CHEMABS 'Online! chemical abstracts service, columbus, ohio, us; Retrieved from STN Database access n°. 46:50661, HAGIWARA AKIMASA ET AL.: "Adhesive film from animal and vegetable proteins" XP002172016 abstract & JP 25 000871 A (HONEN OIL MANUFACTURING CO.) 31 March 1950 (1950-03-31)</p> <p>---</p>	1
A	<p>BE 425 585 A (INTERNATIONAL PATENTS DEVELOPMENT COMPANY) 28 February 1938 (1938-02-28)</p> <p>-----</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 25000871	A	NONE	
BE 425585	A	NONE	